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厦 门 大 学

博 士 后 研 究 工 作 报 告

全球变化下陆-海物质通量研究

——以台湾海峡两岸河流-河口系统溶解有机物为例

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工作完成日期：2015 年 5 月

报告提交日期：2015 年 5 月

厦门大学

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Land-ocean material flux under global changes
--Dissolved organic matter in the river-estuarine systems across Taiwan Strait as examples

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研究工作起始时间 2012 年 11 月

研究工作期满时间 2015 年 5 月

厦 门 大 学

2015 年 5 月

厦门大学博士后研究工作报告

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内 容 摘 要

陆地向海洋的物质输送是全球物质循环的重要环节。在全球变化的背景下，暴雨事件与人为活动对陆-海物质通量的影响在加剧，并进而影响海洋生态系统与生物地球化学过程。陆-海溶解有机物通量是连接陆地与海洋两大生态系统的重要过程。本报告以台湾海峡两岸河流-河口系统为例，针对当前存在的科学问题，除了绪论与结语外，报道以下方面的研究：

第 2 章，以典型亚热带河流九龙江为例，研究夏季暴雨事件对河流溶解有机物的含量与输出通量的显著影响，并通过光谱学方法分析溶解有机物化学组成的变化特征；

第 3 章，针对存在典型最大浑浊带的九龙江河口，系统研究从淡水端到海洋端可溶性有色颗粒有机物的动态变化，并根据实验室模拟实验结果探讨吸附-解吸过程与微生物降解过程对有色溶解有机物含量与化学组成的影响；

第 4 章，以台湾地表河口为研究对象，分析山地型河流的溶解有机物特征及其与流域特征的相关关系，以及河口区溶解有机物含量与化学组成的动态变化；

第 5 章，选取台湾受污水影响程度不同的两个典型地下河口，研究地下河口区溶解有机物的混合行为，并通过微生物降解实验探讨地下河口来源的溶解有机物的生物可利用性。

关键词： 溶解有机物；暴雨事件；陆海界面；地下河口

Abstract

The land-ocean flux is an important component of global material cycle. The impacts of storm events and human activities on land-ocean material flux are enhanced under global changes, which would further affect marine ecosystems and biogeochemical processes. The land-ocean flux of dissolved organic matter is a critical linkage between terrestrial and ocean ecosystems. Besides preface and conclusions, this report takes river-estuarine systems across Taiwan Strait as examples to address a series of scientific questions, including:

Chapter 2, for a typical subtropical river-the Jiulong River, the influences of a summer storm event on the concentration and export flux of dissolved organic matter are studied, along with the changes in the chemical composition of dissolved organic matter as indicated by spectroscopic properties;

Chapter 3, for the Jiulong River Estuary with a typical turbidity maximum zone, the dynamics of dissolved organic matter are systematically investigated from the freshwater end to the marine end, and the effects of sorption-desorption and microbial degradation are discussed based on laboratory incubation experiments;

Chapter 4, for the surface estuaries of Taiwan, the relationship between dissolved organic matter and watershed characteristics in mountainous rivers is revealed, as well as the changes in the concentration and chemical composition of dissolved organic matter in the estuarine environments;

Chapter 5, for two typical subterranean estuaries with different pollution degrees in Taiwan, the mixing behaviors of dissolved organic matter are examined, and the bioavailability of dissolved organic matter from subterranean estuaries is discussed based on microbial incubation experiments.

Keywords: dissolved organic matter; storm event; land-ocean interface; subterranean estuary

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1. 绪 论

1.1. 全球变化下的陆−海物质通量

陆地向海洋的物质输送是海洋物质的重要来源，也是全球物质循环的重要环节。全球入海河流的年径流量约为 3.8×10^{13} m^3，淡水输入是影响近海环流结构及海洋水量平衡的重要因素。同时，河流携带大量泥沙、碳、营养盐和其它各种化学元素进入海洋，对海岸线变迁、近海水体透光度、海洋碳埋藏、海气 CO_2 交换、海洋生产力及其它各种化学元素循环具有重要意义。陆地与海洋之间的物质通量估算在评估陆海相互作用、全球物质循环模式等方面具有重要的研究意义，也是不少国际研究计划长期关注的焦点（例如，LOICZ，海岸带陆海相互作用计划）。

特别地，在全球变化的大背景下，部分地区的暴雨事件的发生频率与强度可能增加，这种变化将对陆-海物质通量的时空分布产生显著的干扰（Liu et al. 2009; Park et al. 2010）。例如，短期的暴雨事件中可能输出大量的陆源物质，其化学组成也可能发生显著的改变，从而使河口、近海等水体的生物地球化学循环发生显著改变，对生态系统产生强烈的脉冲式干扰（Yoon and Raymond 2012; Dhillon and Inamdar 2013; McLaughlin and Kaplan 2013; Bianchi et al. 2013）。其次，各种人类活动（森林砍伐、水坝修筑、农业活动、化肥使用、污水排放等）正在显著改变陆-海物质通量。长期以来人类对森林的砍伐使水土保持能力下降，入海泥沙量比人类活动以前有显著的增加，而水坝的修筑则将大量的泥沙保存在堤坝之后（Syvitski et al., 2005）；化肥使用与污水排放则使陆-海营养盐通量大为升高，提高近海的营养盐水平和生产力，可能导致近海赤潮的发生与生物群落结构的改变（Sanderson et al.,2002; Diaz & Rosenberg, 2008）。最后，全球变暖不仅使极地与高山的冰川融化退缩，也对陆-海物质通量产生显著的干扰，特别是在极地区域的影响更加强烈，冰融初期大量的陆源物质进入海洋，并可对海洋生态系统与物质的生物地球化学循环造成显著影响，引起国际科学界的关注（Hood et al., 2009; Vonk et al., 2012, 2013）。

1.2. 陆-海界面的溶解有机物研究

溶解有机物（Dissolved Organic Matter, DOM）是指能通过一定孔径的滤膜的有机物，研究者一般使用 0.2~1.0 μm 孔径的滤膜来分离溶解态和颗粒态有机物（Benner, 2002）。DOM 含有碳、氢、氧、氮、磷、硫等化学元素，是由许多化合物组成的混合物（Stubbins et al., 2012）。DOM 广泛存在于河流、湖泊、河口和海洋等水体中，是水体中储量最大的还原态碳库，并且在一系列的生物地球化学过程中起着重要作用（Benner, 2003; Battin et al., 2008; Jiao et al., 2010）。例如，DOM 中含有碳元素和氮、磷等营养盐元素，可以通过 DOM 的光降解与微生物降解过程释放出来，构成溶解无机碳及 CO、CO_2 等温室气体、无机氮和无机磷的一个来源，从而影响水体与大气之间的碳交换以及浮游植物的初级生产（Moran and Zepp, 1997; Stedmon et al., 2007; Battin et al., 2008; Lonborg and Sondergaard, 2009; White et al., 2010; Bauer and Bianchi, 2011）。DOM 是微生物异养过程的能量来源和微食物环的物质基础，而微生物把活泼 DOM 转化为惰性 DOM 的过程是水体储存碳的重要途径之一（Benner, 2003; Jiao et al., 2010）。一部分 DOM（即有色溶解有机物，Chromophoric Dissolved Organic Matter，CDOM）既能强烈吸收紫外光，从而保护水生生物免受紫外线损害，又会吸收光合作用有效能量区域的光，从而影响浮游植物的光合作用和初级生产力（Coble, 2007）。

以 DOC 计，全球河流向海洋输送的 DOM 通量多达每年 2.1~2.5 亿吨碳，构成了连接陆地与海洋两大生态系统的重要纽带，是影响陆海界面水体中碳与营养元素循环、水环境光学性质与初级生产力的重要因素（Ludwig et al., 1996; Hedges et al., 1997; Chen, 2004; Battin et al., 2008; Dai et al., 2012）。河流 DOM 的动态变化受到许多因素的影响，例如水文条件、地理背景、土地利用、絮凝与吸附-解吸过程、光化学过程与微生物降解等（Hood et al., 2006; Jaffé et al., 2008; Huang and Chen, 2009; Williams et al., 2010; Spencer et al., 2010; Yamashita et al., 2010, 2011; Cawley et al., 2012; Hong et al., 2012）。在全球变化的背景下，暴雨事件对河流 DOM 的含量与化学组成产生强烈影响（Hood et al., 2006; Wiegner et al., 2009; Raymond and Saiers, 2010; Yoon and Raymond 2012; Dhillon and Inamdar 2013）。此外，暴雨事件下河流 DOM 的生物可利用性也可能发生显著改变（Wiegner et al., 2009; Fellman et al., 2009）；暴雨事件下 DOM 输出的增加可以使微生物活动加强（Klug et al. 2012; McLaughlin and Kaplan 2013）、使下游水体的 CO_2 含量升高、

从而影响水-气 CO_2 交换（Bianchi et al. 2013）。

除了流域自然条件、极端天气事件与人为活动，河口区生物地球化学过程对陆-海溶解有机物通量与生物地球化学的影响也不可忽视。河口的物理、化学和生物学梯度非常显著，是动力学过程非常活跃的一个界面（Dagg et al., 2004; Bianchi, 2007; Bauer and Bianchi, 2011）。河口区的一系列生物地球化学过程将改变最终到达海洋的陆源溶解有机物的通量、化学组成与反应活性（Shank et al., 2010; Guo et al., 2011; Osburn et al., 2012）。这些过程包括人为活动来源、盐沼与自生源的有机物的添加过程，以及颗粒物的吸附、微生物降解与光化学降解等去除过程（Spencer et al., 2007; Shank et al., 2010; Bauer and Bianchi, 2011）。即使在 DOM 含量呈现表观保守行为的河口，DOM 中的不同组分也可能呈现不同的河口行为、从而改变输入到海洋的 DOM 的化学组成与生物地球化学活性（Yamashita et al., 2008; Guo et al., 2011）。

1.3. 当前存在的科学问题

国内外的研究在陆-海界面溶解有机物的动态变化与生物地球化学上取得了大量成果，但是仍存在一些科学问题有待解决：

（1）近年的许多研究是针对温带和高纬度河流开展的，但热带、亚热带河流对全球陆-海 DOM 通量的贡献却更大、可达到 60%左右，因此热带、亚热带河流的 DOM 研究对于全面理解陆-海 DOM 通量与生物地球化学具有很重要的意义（Spencer et al., 2010; Ludwig et al., 1996; Huang et al., 2012）。特别地，中国东部可受到台风的强烈影响，期间的暴雨事件可能对陆-海界面的 DOM 通量与化学组成产生强烈的脉冲式干扰，但是相关研究很少。

（2）在浑浊河口，有机物在溶解态与颗粒态之间的分配是一个重要的过程（Uher et al., 2001; Shank et al., 2005; Shank et al., 2011; Pisani et al., 2011），但是，很少研究分析从淡水端到海洋端的完整体系中的水溶性颗粒态有色有机物（water-soluble chromophoric particulate organic matter，CPOM， Osburn et al., 2012），因而限制了对于固相-液相有色有机物分配的理解。

（3）许多山地小河流（流域面积< 10,000 km^2 并且源头海拔> 1,000 m）位于热带区域的南亚与大洋洲，并且在陆-海沉积物和颗粒态有机碳通量中扮演重要角色（Milliman and Syvitski, 1992; Lyons et al., 2002）。很少研究针对这些河流及

其河口中DOM的动态变化，因而流域特征及相关河流过程对这些山地河流DOM的含量与输出的影响、DOM 在这些河流的河口区的含量、化学组成及生物地球化学活性变化等问题仍存在很多未知。

（4）在陆-海界面的 DOM 研究上，地表河流的研究相对比较充分，而地下水的研究方兴未艾。目前科学界已经发现地下水在淡水与营养盐的输送入海中起着重要作用（Moore, 1996, 1999; Zhang and Satake, 2003; Burnett et al., 2003, 2006; Moore et al., 2008; Peng et al., 2008），而关于 DOM 的研究则还较少。特别地，在淡水地下水与海水混合形成的地下河口，水体停留时间长并且微生物降解与固相-液相分配过程活跃（Moore, 1999），但关于地下河口 DOM 的河口行为与生物可利用性的了解仍然比较有限（Santos et al., 2008, 2009; Kim et al., 2012, 2013）。

1.4. 本论文的研究内容

本研究以台湾海峡两岸的河流-河口系统为典型研究对象，针对上述科学问题开展研究，并总结发表博士研究生与博士后期间的成果，内容如下：

（1）第 2 章：以典型的亚热带河流九龙江为例，研究夏季暴雨事件对河流 DOM 含量与化学组成的影响；

（2）第 3 章：以九龙江河口为例，研究从淡水端到海洋端 CPOM 的动态变化，并比较 CPOM 与 CDOM、水溶性沉积态有机物（water-soluble chromophoric sediment organic matter，CSOM）的化学组成异同，以评估河口区吸附-解吸作用在 CDOM 非保守行为中的作用；

（3）第 4 章：以山地型河流众多、人口密集的台湾西部河流为例，研究流域特征对台湾河口淡水端 DOM 含量的影响，以及 DOM 组分在河口区的动态变化；

（4）第 5 章：以两个受污水影响差异非常显著的地下河口为例，研究地下河口中 DOM 的混合行为与生物可利用性。

2. 夏季暴雨事件对典型亚热带河流溶解有机物通量与组成的影响

2.1. Introduction

Dissolved organic matter (DOM) is the largest pool of reduced carbon and plays important roles in a variety of biogeochemical processes and ecosystem function in aquatic environments (Benner, 2003). For example, abundant carbon and nutrient elements (such as nitrogen and phosphorus) are bound within DOM, which can be released as CO_2 and bioavailable inorganic nutrients upon the decomposition of DOM (e.g., Moran and Zepp, 1997; Stedmon et al., 2007; Lonborg and Sondergaard, 2009). The speciation, solubility, bioavailability and toxicity of metals are also affected by DOM (e.g., Sánchez-Marín et al., 2010; Hassler et al., 2011). The microbial utilization of DOM is the start of the microbial food loop, while the microbial transformation of labile DOM to refractory DOM can store carbon for thousands of years in the ocean (Jiao et al., 2010). Chromophoric DOM (CDOM), which absorbs both photosynthetically active and ultraviolet radiation, affects both primary production and the habitat for organisms (Coble, 2007). The biogeochemical reactivity of DOM is largely dependent on its chemical composition. For example, the bioavailability of DOM is related to its molecular weight (Loh et al., 2004) and the fraction of protein-like materials (Fellman et al., 2009, 2010a, b). Different constituents of DOM have variable photochemical reactivity (Kieber et al., 2007; Spencer et al., 2009; Stubbins et al., 2010). Therefore, to better understand the biogeochemical role of DOM, it is important to examine both the concentration and composition of DOM in aquatic environments.

Annually, approximately 0.2~0.25 Gt C of DOM is transported by global rivers to the ocean (Ludwig et al., 1996; Battin et al., 2008), which represents an important biogeochemical linkage between the terrestrial and marine ecosystems. Recent studies have focused disproportionately on temperate and high-latitude rivers, but tropical rivers contribute more to the global land-ocean flux of dissolved organic carbon (DOC) (Spencer et al., 2010; Ludwig et al., 1996). In addition, our understanding of

本章内容发表在《Applied Geochemistry》2013 年 28 卷 164-171 页.

DOM dynamics in tropical rivers is largely limited to a few large systems (e.g. Mayorga et al., 2005; He et al., 2010), and the factors that control the concentration, composition and flux of DOM in many other medium-sized and small rivers requires further study. In fact, the biogeochemistry of DOM in rivers can be affected significantly by many factors such as hydrological condition, geological settings, land use, microbial activity and photo-degradation (e.g. Hood et al., 2006; Williams et al., 2010; Yamashita et al., 2010, 2011; Cawley et al., 2012; Hong et al., 2012).

In particular, the concentration, composition and flux of DOM can change greatly during extreme storm events. For example, the DOC concentration increases by approximately threefold and the proportion of humic DOM increases in a storm event in three small watersheds, Oregon (Hood et al., 2006). The mean concentration and flux of DOC at stormflow are 2.2 and 57 times higher than those at baseflow in the Wailuku River, Hawaii (Wiegner et al., 2009). Storm and snow melt events together accounts for ~86% of DOC export in 30 small forested watersheds in the eastern US, and one critical area of future research is to study compositional changes of DOM during these events (Raymond and Saiers, 2010). The protein-like fraction in total fluorescence and the bioavailability of DOM decrease in an upland watershed but increase in a wetland dominated watershed during stormflows in Alaskan Rivers (Fellman et al., 2009). To better evaluate the biogeochemical role of DOM in linking the terrestrial and marine ecosystems, it is important to study the flux and composition of DOM during storm events, in particular considering that most studies have focused on DOM under baseflow conditions and that the frequency of heavy precipitation events is likely to increase in the future due to climate change (IPCC, 2007).

Absorption and fluorescence spectroscopy are useful for characterizing the concentration and composition of DOM. Absorption coefficient and fluorescence intensity are indicators for the levels of CDOM and fluorophores, while carbon specific CDOM absorption coefficient at UV ($SUVA_{254}$), and absorption spectral slope ratio (S_R) are valuable proxies for the composition of DOM (Weishaar et al., 2003; Helms et al., 2008). Fluorescence excitation emission matrix spectroscopy coupled with parallel factor analysis (EEMs-PARAFAC) provides a powerful tool in differentiating fluorescent components and in tracing their dynamics (e.g., Stedmon and Markager, 2005a; Kowalczuk et al., 2009; Fellman et al., 2010a; Chen et al., 2010; Yang et al., 2012a; Maie et al., 2012). Only recently have a very few studies applied fluorescence spectroscopy to study DOM dynamics in storm events and they were limited to mid-high latitude rivers (Fellman et al., 2009; Austnes et al., 2010; Nguyen et al., 2010). Studies are required to assess the potential of such techniques with respect to DOM dynamics in tropical watersheds.

The Jiulong River is a subtropical river located in southeastern China, with distinct dry and wet seasons under the influence of the East Asian Monsoon (Hong et al., 2012). Tropical storms violently impact this area several times per year and bring heavy precipitations, which may lead to rapid flushing of DOM from the land to the ocean. The effects of storm events on the level and composition of DOM is poorly studied for not only the Jiulong River but also many other rivers in this region including some large ones such as the Yangtze River and the Pearl River (Fig. 2-1). Although a higher DOM concentration and a lower protein-like fraction in total fluorescence have been observed after storms than in the dry season in our five basin scale investigations (Hong et al., 2012), dynamics of DOM at high temporal resolution in a storm event with changing flow is unknown. This study aimed to examine the temporal changes in the flux and composition of DOM in a summer storm event, using DOC, absorption spectroscopy and EEMs-PARAFAC.

2.2. Materials and methods

2.2.1. Study area

The Jiulong River is a subtropical river located in Fujian province, southeastern China, with a drainage area of 14,741 km^2. The mean annual temperature and precipitation are 19.9~21.1 ℃ and 1400~1800 mm (Yang et al., 2012b). The main land cover of the watershed is forestland (69.4%) and arable land (18.4%) (Huang et al., 2011). There are three major tributaries in the watershed: North River, West River and South River (Fig. 2-1). The North River is the main tributary with a length of 274 km, a drainage area of 9,803 km^2 (accounting for 66.5% of the total area of the Jiulong River watershed) and a mean annual discharge of 82.3×10^8 m^3 (with ~74% occurring in the wet season from April to September).